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(54) Title: COSMETIC COMPOSITIONS WITH THERMOCHROMIC COLOR CHANGE SUBSTANCES AND AN AGENT FOR INDUCING A TEMPERATURE CHANGE

(57) Abstract: The present invention provides a cosmetic composition, which comprises an agent that is capable of reacting with water to cause a change in the temperature of the composition, a thermochromic substance and a pharmaceutically acceptable carrier. When applied to the skin, the composition extracts moisture or is wetted causing the agent to react thereby changing the temperature of the composition. The change in temperature induces the thermochromic substance to impart a different colour to the composition. A user is thereby notified by this sensorial signal that the cosmetic composition has completed its intended treatment and/or brought about a change in the condition of the skin.

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COSMETIC COMPOSITIONS WITH THERMOCHROMIC COLOR CHANGE  
SUBSTANCES AND AN AGENT  
FOR INDUCING A TEMPERATURE CHANGE

5

**BACKGROUND OF THE INVENTION**

**Field of the Invention**

10 The present invention relates to cosmetic compositions that provide consumers with a colour change indicator as a sensorial signal.

**The Related Art**

15

Cosmetics are often provided with consumer perceivable sensorial signals. Most common of these signals are fragrances. Pleasing odour is often the single most important attribute inducing re-purchase by a consumer.

20 Other sensorial attributes are also significant in cosmetic chemistry. Skin-feel of a product is highly important. Creams, lotions, gels and pastes are often judged for their efficacy by the tactility of their feel. Silky, non-residue leaving cosmetics are much preferred over tacky ones, and

25 the consumer may relate those aesthetics to actual pharmacological performance.

Sometimes the sensorial attribute is that of temperature. Coolness is imparted to toothpastes and aftershave lotions

30 through the presence of camphor, menthol or menthol derivatives such as menthol lactate. Some formulations

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signal efficacy through a temperature increase. Inclusion of capsaicin, an alkaloid extracted from capsicum, gives a brief temperature rise sensation to the human neural system.

- 5 Exothermic and endothermic reactions are other sources of temperature signalling. U.S. Patent 5,861,440 (Gohla et al.) describes the use of sugars, especially xylitol, for inducing a cooling sensation when contacted with water. Generation of exothermic heat is reported in U.S. Patent  
10 4,379,143 (Sherry et al.), U.S. Patent 4,626,550 (Hertzenberg), U.S. Patent 4,362,715 (Strianse et al.) and U.S. Patent 3,250,680 (Menkart et al.). Each of these documents describes the use of an aluminosilicate interacting with water to release momentary heat.
- 15 U.S. Patent 5,747,202 (Slavtcheff et al.) discloses a fast drying peelable facial mask formulation based upon a combination of polyvinyl alcohol and hydrophobically modified acrylates. This mask is representative of a class  
20 of cosmetics requiring a finite maturing time for the product to set as a hardened film. Consumers would find a mechanism for indicating that the cosmetic has matured, such as a colour change, useful.
- 25 One commercial embodiment of a colour change signal is the Biore® Self Heating Mask. The product lists the following ingredients: butylene glycol, sodium silico aluminate, kaolin, PEG-8, methyl gluceth-20, hydroxypropyl cellulose, dimethicone, hydroxypropyl methylcellulose, talc, acrylates  
30 copolymer, polyethylene and minor ingredients including encapsulated ultramarine pigments. Instructions on use of

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the product require wetting of the face which when contacted with the Biore® product causes self-heating by reaction of water with the silico aluminates and kaolin. The composition is applied by rubbing across the face. Massage  
5 through the rubbing action breaks the encapsulating material, releasing the ultramarine pigments thereby turning the composition a uniform blue colour. Once developed, the blue color signals the consumer it is time to rinse away the product. In this system the ultramarine colouring mechanism  
10 is unrelated to the heating phenomena. A drawback of this system is the requirement for actual physical breakdown of walls encapsulating the colorant. This procedure is messy and requires an active manipulation.

15 Other types of sensorial signals have been sought for incorporation into cosmetics. The signals should either provide an independently new effect or complement those that have traditionally been employed.

20 Accordingly, it is an advantage of the present invention to be able to provide cosmetic products, with a new sensorial signal.

Another advantage of the present invention is to be able to  
25 provide cosmetic products with a combination sensorial signal employing a temperature change triggering an alteration of colour.

Another advantage of the present invention is to be able to  
30 provide cosmetic products having a timing mechanism for

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application, for rub-in or for removal of the product from a consumer's skin.

These and other advantages of the present invention will become more readily apparent from consideration of the following summary and detailed discussion.

#### **SUMMARY OF THE INVENTION**

The present invention provides a cosmetic composition which comprises:

- (i) an agent which interacts with water to cause a change in the temperature of the cosmetic composition;
- (ii) a thermochromic substance which changes color in response to the change of temperature; and
- (iii) a pharmaceutically acceptable vehicle for delivering the agent and the thermochromic substance to a user's skin.

#### **DETAILED DESCRIPTION OF THE INVENTION**

The present inventors have found a visual sensorial combination of signals, which is suitable for use with cosmetic products. The present invention relates to a product to be applied to the skin and containing an agent which reacts with water to generate a temperature change and a thermochromic substance which alters its colour responsive to the temperature change. Water of activation is preferably placed on an area of the skin to be treated by

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the product or mixed with a product just prior to application. Less desirable, but also quite useful, is use of the inherent moisture and sweat found on surfaces of the skin.

5

The thermochromic substances used in the present invention have one colour at room temperature but undergo a colour change at either higher or lower temperatures. Examples of such substances include double salts comprising a transition metal such as cobalt, nickel or manganese in combination with an aminic amide such as hexamethylenetetramine. These double salts discolour on releasing water when heated and resume the original colour on absorption of moisture when cooled. Other examples include mercury iodide, double complex salts of mercury iodide with other metallic iodides, heavy metal compounds such as lead chromate and ammonium metavanadate, dixanthylene and bianthrone. These types of materials can all be used in the present invention but are not the most preferred materials.

20

Particularly preferred thermochromic substances are substances based on ink technology.

The amount of the thermochromic substances used may range from about 0.00001 to about 10%, preferably from about 0.01 to about 2%, more preferably from about 0.1 to about 1%, optimally from about 0.5 to about 0.8% by weight of the cosmetic composition.

Thermochromic substances based on ink technology typically comprise: (1) an acid-responsive chromogenic material; and

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- (2) an acidic material; optionally combined with (3) a solvent for dilution of the other materials. The acid-responsive chromogenic material in the thermochromic substance may include triphenylmethanephthalide compounds, phthalide compounds, phthalan compounds, acyl-leucomethylene blue compounds, fluoran compounds, triphenylmethane compounds, diphenylmethane compounds and spiropyran compounds.
- 10 Examples of suitable acid-responsive chromogenic materials include the following:
- 3,6-dimethoxyfluoran (yellow), 3,6-dibutoxyfluoran, 3-diethylamino-6,8-dimethylfluoran, 3-chloro-6-phenylaminofluoran (orange), 3-diethylamino-6-methyl-7-chlorofluoran (vermilion), 3-diethylamino-7,8-benzofluoran (pink), 2-anilino-3-methyl-6-diethylamino-fluoran (blue), 3,3',3''-tris(p-dimethylaminophenyl)phthalide (purplish blue), 3,3'-bis(p-dimethylaminophenyl)phthalide (green), 3-diethylamino-7-phenylaminofluoran (black), 3,3-bis(p-diethylaminophenyl)-6-dimethylaminophthalide, 3-(4-diethylaminophenyl)-3-(1-ethyl-2-methylindol-3-yl)phthalide, 3-(4-diethylamino-2-methyl)phenyl-3-(1,2-dimethylindol-3-yl)phthalide, 2'-(2-chloroanilino)-6'-dibutylaminospiro-[phthalido-3,9'-xanthene] and mixtures thereof. The acid-responsive chromogenic material is typically used in an amount from about 0.1 to about 50% by weight of the thermochromic substance.

- The acidic material mentioned may include 1,2,3-benzotriazole compounds, phenol compounds, thiourea compounds, oxo-aromatic carboxylic acids and mixtures

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thereof. Specific examples include: 1,2,3-benzotriazole, 1,2,3-triazole ethyl 4-methyl-5-carboxylate, 4(5)-hydroxy-1,2,3-triazole, 5(6)-methyl-1,2,3-benzotriazole, 5(6)-chloro-1,2,3-benzotriazole, 5(6)-methoxy-1,2,3-  
5 benzotriazole, 4(7)-nitro-1,2,3-benzotriazole, 5(6)-carboethoxy-1,2,3-benzotriazole, 5-methoxy-7-nitro-1,2,3-benzotriazole, 4-amino-1,2,3-benzotriazole, 4-benzoylamino-1,2,3-benzotriazole, 4,5,6,7-tetrachloro-1,2,3-benzotriazole, 4-hydroxy-1,2,3-benzotriazole, naphtho-1,2,3-  
10 benzotriazole, 5,5'-bis-1,2,3-benzotriazole, 4(7)-sulfoanilino-1,2,3-benzotriazole, 1,2,3-triazole diethyl dicarboxylate, phenol, nonylphenol, bisphenol A, bisphenol F, 2,2'-biphenol, beta-naphthol, 1,5-dihydroxynaphthalene, alkyl p-hydroxybenzoates, phenol resin oligomer and mixtures  
15 thereof. The acidic material is typically used in an amount of about 0.1 to about 50% by weight of the thermochromic substance.

The thermochromic substances, each containing an acid-responsive chromogenic material and an acidic material, are preferably diluted with a solvent before use. The use of a solvent renders the substance responsive to changes in temperature with greater sensitivity and definition. The solvents which can be used for the thermochromic substance  
25 includes, among others, C<sub>8</sub>-C<sub>40</sub> alcohols, alcohol-acrylonitrile adducts, azomethine compounds, esters and mixtures of these. Specific examples of suitable solvents include decyl alcohol, lauryl alcohol, myristyl alcohol, cetyl alcohol, stearyl alcohol, behenyl alcohol, lauryl  
30 alcohol-acrylonitrile adduct, myristyl alcohol-acrylonitrile adduct, stearyl alcohol-acrylonitrile adduct, benzylidene-p-



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toluidine, benzylidene-butylamine, octyl caprate, decyl caprate, myristyl caprylate, decyl laurate, lauryl laurate, myristyl laurate, decyl myristate, lauryl myristate, cetyl myristate, lauryl palmitate, cetyl palmitate, stearyl palmitate, cetyl myristate, lauryl palmitate, cetyl palmitate, stearyl palmitate, cetyl p-t-butylbenzoate, stearyl 4-methoxybenzoate, dilauryl thiodipropionate, dimyristyl thiodipropionate, stearyl benzoate, benzyl stearate, dibenzyl thiodipropionate, distearyl thiodipropionate, benzyl benzoate, glycerol trilaurate and mixtures thereof. The amount of the solvent used may range from 0 to about 90%, preferably from about 0.1 to 50% by weight of the thermochromic substance.

Reversibly variable colour thermochromic substances can optionally be microencapsulated before incorporation into the cosmetic product. Microencapsulation can be accomplished in any conventional manner. For example, the desired microcapsules can be prepared in water by any of interfacial polymerization, in situ polymerization, coacervation, air suspension, interfacial precipitation and other techniques using the reversibly variable colour material, a shell-forming polymer and, where necessary, a surfactant, protective colloid, pH control agent, electrolyte, etc. Microcapsules with particle sizes of from about 1 to 50  $\mu\text{m}$  in diameter can be obtained by such processes. It is also possible to provide double- or multiple-walled microcapsules by using one, two or more of the microencapsulation techniques mentioned above. The preferred shell-forming material includes a polyamine and a carbonyl compound for forming a polyurea shell, a polybasic

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acid chloride and a polyamine for forming a polyamide shell, a polyisocyanate and a polyhydroxy compound for forming a polyurethane shell, a polybasic acid chloride and a polyhydroxy compound for forming a polyester shell, an epoxy compound and a polyamine for forming an epoxy resin shell, a melamine-formaldehyde prepolymer for forming a melamine resin shell and a urea-formaldehyde prepolymer for forming a urea resin shell, as well as ethylcellulose, polystyrene, polyvinyl acetate and so on.

10

The above information with respect to the ink based thermochromic substances may be found in U.S. Patent 4,717,710, U.S. Patent 4,851,282 and U.S. Patent 5,431,697, all herein incorporated by reference. Substances described therein, or at least similar substances are available from the assignee, Matsui International Company, Inc., Gardena, California. A substance commercially available from Matsui International and suitable for use in the present invention is Chromicolor AQ Ink, especially Type 27 which is available in twelve colours. Type 27 has a colour appearing below 24°C and changing above 33°C. Thus, a blue variant of Type 27 will be blue until heated by an exothermic reaction between the water reactive agent and a water source. As the temperature rises, the blue will fade to colourless and eventually return to blue when the system has cooled. Other useful Chromicolor AQ Inks are Type 35 where colour is maintained below 27°C and disappears above 36°C. Type 25 has colour appearing below 22°C but disappearing above 31°C. Endothermic reactions may usefully employ Type 07 where the

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system is colourless above 5°C but colour appears below minus 4°C.

The compositions of the present invention comprise an agent  
5 that can interact with water to generate a change of  
temperature. This agent is typically admixed with the  
cosmetic composition. Suitable agents should be capable of  
causing an exothermic or endothermic temperature jump in the  
composition of at least about 2°C, preferably from about 5°  
10 to about 30°C, more preferably from about 8° to about 20°C,  
even more preferably from about 10° to about 15° C.

Illustrative examples of the exothermic reaction inducing  
agents are dry forms of silica, activated alumina,  
15 aluminosilicates and combinations thereof. Particularly  
preferred are synthetic aluminosilicates such as Zeolite A  
available from PQ Corporation and Cab-O-Sil® fumed silica  
available from the Cabot Corporation. Alternatively, a  
redox type reaction can be employed to generate heat.  
20 Examples of endothermic agents are ammonium chloride and  
xylitol. The amount of these agents used may range from  
about 1 to about 70%, but usually from about 25 to about  
60%, optimally from about 35 to about 50% by weight. When  
incorporating a water sensitive temperature change inducing  
25 agent, care must be taken to maintain the product within  
packaging (e.g. sealed pouch or packet) that avoids exposure  
to moisture or at least excessive moisture before use. On  
use or just prior to use, the composition is subjected to

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water, and this generates the appropriate temperature change.

A variety of skin conditioning and protective agents may be formulated with the cosmetic compositions of the invention. Many of these may be considered also as pharmaceutically acceptable carriers. These agents may include moisturisers, preservatives, herbal extracts, vitamins, anti-irritant agents, emulsifiers and keratolytic agents.

10

Polyhydric alcohols, also known as polyols, are the most useful moisturizers. Representative polyols include glycerine, diglycerine, propylene glycol, dipropylene glycol, polypropylene glycol, polyethylene glycol and derivatives thereof, sorbitol, hydroxypropyl sorbitol, hexylene glycol, 1,2-butylene glycol, 1,2,6-hexanetriol, isoprene glycol, 2-methyl-1,3-propanediol, ethoxylated glycerol, propoxylated glycerol and mixtures thereof. The amount of polyol used may range from about 0.1 to about 95%, preferably from about 1 to about 50%, more preferably from about 1.5 to about 20%, optimally from about 3 to about 10% by weight of the cosmetic composition.

20

Preservatives can be incorporated into the compositions to protect against the growth of potentially harmful microorganisms. Suitable preservatives include alkyl esters of para-hydroxybenzoic acid, hydantoin derivatives, propionate salts, and a variety of quaternary ammonium compounds. Cosmetic chemists are familiar with appropriate preservatives and routinely choose them to satisfy the preservative challenge test and to provide product

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stability. Particularly preferred preservatives are phenoxyethanol, methyl paraben, propyl paraben, imidazolidinyl urea, sodium dehydroacetate and benzyl alcohol. Preservatives are preferably employed in an amount  
5 ranging from about 0.01% to about 2% by weight of the composition.

Herbal extracts may include Roman Chamomile, Green Tea, Scullcap, Nettle Root, Swertia Japonica, Fennel, Anise,  
10 Arnica, Calandula, Coltsfoot, Cornflower, Elder, Gentian, Hawthorn, Lavender, Linden, Myrrh, Oat, Rose, Sweet Clover, Sandalwood, Vetiver, Tulsi, Kamala, Eucalyptus, St. John's Wort and Aloe Vera extracts. The amount of each of the extracts may range from about 0.00001 to about 1%,  
15 preferably from about 0.01 to about 0.5%, optimally from about 0.05 to about 0.2% by weight of the composition.

Vitamins useful in products of the present invention include vitamin E acetate, vitamin C, vitamin A palmitate, panthenol  
20 and any of the Vitamin B complexes. Anti-irritant agents may also be present including those of alpha-bisabolol and potassium glycyhrrizinate, each vitamin or anti-irritant agent typically being present in an amount ranging from about 0.001 to about 0.5%, preferably from about 0.01 to  
25 about 0.1% by weight of the composition.

Emulsifiers may also be incorporated into the cosmetic compositions of the present invention. These emulsifiers may be anionic, nonionic, cationic or amphoteric emulsifiers  
30 or a combination thereof. Useful nonionic type emulsifiers include the C<sub>10</sub>-C<sub>20</sub> fatty alcohols or acid hydrophobes

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condensed with from 2 to 100 moles of ethylene oxide or propylene oxide per mole of hydrophobe; C<sub>2</sub>-C<sub>10</sub> alkyl substituted phenols condensed with from 2 to 20 moles of alkylene oxide; mono- and di-fatty acid esters of ethylene glycol; fatty acid monoglyceride; sorbitan, mono- and di-C<sub>8</sub>-C<sub>20</sub> fatty acids; block copolymers (ethylene oxide/propylene oxide); and polyoxyethylene sorbitan as well as combinations thereof. Alkyl polyglycosides and saccharide fatty amides (e.g. methyl gluconamides) are also suitable nonionic emulsifiers. The amount of emulsifier used may range from about 0.1 to about 30%, preferably from about 0.5 to about 10% by weight of the composition.

Keratolytic agents may be incorporated into the compositions. Typical of these agents are alpha and beta hydroxycarboxylic acids. The alpha-hydroxycarboxylic acids include glycolic acid, malic acid, lactic acid and mixtures thereof as well as their salts such as alkali metal and ammonium salts. The most preferred beta hydroxycarboxylic acid is salicylic acid. The amount of these keratolytic agents may range from about 0.01 to about 15%, preferably from about 1 to about 8% by weight of the composition.

Among other pharmaceutically acceptable carriers include hydrocarbons, silicones, esters, inorganic powders and a variety of thickening agents. Each of these may be employed at a concentration ranging from about 0.1 to about 98%, preferably from about 1 to about 95%, more preferably from about 5 to about 50%, optimally from about 2 to about 25% by weight of the composition.

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Hydrocarbons suitable as carriers include mineral oil, isoparaffins, polyalphaolefins, petrolatum, polydecenes, polyisobutylene, and microcrystalline polyethylene waxes.

5

Silicones useful as carriers may be volatile or non-volatile. Volatile silicones are low molecular weight and relatively non-viscous linear or cyclic organopolysiloxanes. Most useful are tetramer and pentamer cyclomethicones. Non-volatile silicones include silicone gums such as Dow Corning SE-30 types having molecular weights above 100,000, preferably above 500,000. Fluid polydimethylsiloxanes are commercially available as Dow Corning 200, Dow Corning 550 and the General Electric SF-96 series. Other non-volatiles include polyalkylarylsiloxanes and polyphenylmethylsiloxanes. By "non-volatile" is meant a fluid with a vapour pressure of less than about 10 mm Hg, preferably less than about 1 mm Hg at 30°C. Alkoxylated polydimethylsiloxanes, known as dimethicone copolyols, may also be utilised.

Esters, which can be useful carriers, include those of synthetic or natural origin. Among the natural esters are included triglycerides such as soybean oil, cottonseed oil, sunflower seed oil, carnauba wax, candellia wax and beeswax. Synthetic esters include C<sub>12</sub>-C<sub>22</sub> fatty acid esters of C<sub>1</sub>-C<sub>11</sub> monohydric alcohols, C<sub>12</sub>-C<sub>22</sub> fatty alcohol esters of C<sub>3</sub>-C<sub>11</sub> mono and dicarboxylic acids, mono- and di- glycerides, citrates, and polyalkylene oxides of fatty acids.

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- Thickeners may also be employed as carriers. These include polyacrylamides, polyacrylates, cross-linked polyacrylates such as carbomers, xanthan, carrageenan, pectin, guar gum, 5 sodium carboxymethyl cellulose, hydroxymethyl cellulose, hydroxypropyl cellulose, ethyl cellulose, hydroxypropyl methylcellulose, polyoxyethylene-polyoxypropylene block copolymers and mixtures thereof.
- 10 Inorganic powders suitable as carriers include titanium dioxide, zinc oxide, sodium sulfate, calcium carbonate, magnesium silicates, iron oxides, talc, mica, bentonites, boron nitrites, kaolin (of a type not generating substantial heat on contact with water), montmorillonites, hectorites, 15 attapulgites and mixtures thereof.

- The cosmetic compositions of the present invention may be in any form. They may be liquids, bars, powders, creams, lotions, sprays, pastes and semi-solid sticks. Product 20 types include but are not limited to facial masks, depilatories, anti-acne products, anti-wrinkle products, skin lightening products, self-tanning products (especially those with dihydroxyacetone and polysaccharides), antiperspirants (utilised with aluminium and/or zirconium 25 astringent salts) and deodorants.

- Except in the operating and comparative examples, or where otherwise explicitly indicated, all numbers in this description indicating amounts of material ought to be 30 understood as modified by the word "about".



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The following Examples will more fully illustrate the embodiments of this invention. All parts, percentages and proportions referred to herein and in the appended claims are by weight unless otherwise indicated.

5

**EXAMPLES 1-6**

Facial warming mask compositions are prepared as pastes having formulas whose ingredients are listed in Table I.

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**TABLE I****Facial Warming Mask**

5

INGREDIENTS	PARTS/WEIGHT					
	1	2	3	4	5	6
<b>Phase A</b>						
Butylene Glycol	40.40	40.40	40.40	40.40	38.40	38.40
Hydroxypropyl Cellulose	0.40	0.70	0.40	0.40	0.40	0.40
Hydroxypropyl Methylcellulose	0.30	--	0.30	0.30	0.30	0.30
Sodium Magnesium Silicate (Laponite XLG)	0.50	0.50	--	--	--	--
Chromiclor AQ Ink (Type 27)	1.02	0.52	0.32	1.02	0.52	0.32
<b>Phase B</b>						
Carbowax PEG 400	4.00	4.00	4.00	4.00	4.00	4.00
Methyl Gluceth-20	0.60	0.60	0.60	0.60	0.60	0.60
Dimethicone Copolyol	0.60	0.60	0.60	0.60	0.60	0.60
<b>Phase C</b>						
Zeolite A	38.00	38.40	38.00	--	--	--
Anhydrous Silica	--	--	--	38.00	38.00	38.00
Titanium Dioxide	0.40	--	0.40	0.40	0.40	0.40
Talc	1.00	1.00	1.00	1.00	1.00	1.00
Kaolin	8.70	8.20	12.90	8.20	12.70	12.90
Anhydrous Silica	--	--	--	--	10.20	10.20
<b>Phase D</b>						
Fragrance	0.80	0.80	0.80	0.80	0.80	0.80
Herbal Extracts	0.25	0.25	0.25	0.25	0.25	0.25
Alpha-Bisabolol	0.03	0.03	0.03	0.03	0.03	0.03

Application of the product involved wetting the face,  
 10 applying the warming mask composition and, with a little  
 added water on the fingers, spreading the mask across the  
 face. After a massage of approximately 60 seconds, the

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thermochromic ingredient turned blue to signal it was time to rinse the mask away with water. The mask was not intended to dry across the face.

5 **EXAMPLE 7**

A keratotic plug removing composition was prepared according to the composition listed in Table II. The composition was applied as an adhesive paste to acne affected areas of the skin. Moisture in the skin reacted with the zeolite, generating heat and thereby activating the thermochromic colorant. After a short period of time, a green colour appeared indicating the paste had set into a hardened film. The user was then signalled to remove the hardened film from the face thereby also pulling plugs and blackheads from within pores of the acne infection.

**TABLE II**

INGREDIENTS	WEIGHT %
Poly(methylvinylmaleic anhydride)	40.0
Zeolite A	40.0
Propylene Glycol	12.4
Aminopropanol	7.0
Chromicolor AQ Ink (Type 27)	0.6

20

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**EXAMPLE 8**

Another keratotic plug removing composition was prepared according to the composition listed in Table III. The composition was applied as an adhesive paste to acne affected areas of the skin. Moisture in the skin reacted with the silica generating heat thereby activating the liquid crystal thermochromic colorant. After a short period of time, a blue colour appeared indicating the paste had set into a hardened film. The user was then signalled to remove the hardened film from the face thereby also pulling plugs and blackheads from within pores of the acne infection.

**TABLE III**

INGREDIENTS	WEIGHT %
Polyvinylformamide	40.0
Anhydrous Silica	40.0
Chromicolor AQ Ink (Type 25)	1.0
Glycerine	19.0

**EXAMPLE 9**

This Example illustrates a depilatory wherein a thermochromic substance changes color to indicate that it is time for removal of the product from the skin. Water was applied to the legs. The depilatory having the formula listed in Table IV was placed on the wet legs. Upon change of color, the depilatory was rinsed from the legs.

**TABLE IV****Depilatory Composition**

5

COMPONENT	WEIGHT %
Polyethylene Glycol	47.0
Zeolite A	40.0
Thioglycolic Acid	5.0
Fragrance	1.0
Hydroxypropyl Cellulose	5.0
Chromicolor AQ Ink	2.0

**Example 10**

- 10 This Example relates to an antiperspirant composition according to the present invention and having a formula as listed in Table V. When applied to the underarm, the formula was wetted from perspiration to activate the silica. Heat was generated and the thermochromic substance changed
- 15 colour to signal activity.

**TABLE V****Antiperspirant Composition**

20

COMPONENT	WEIGHT %
Aluminum Zirconium Chlorhydrate	25.0
Zeolite A	35.0
Stearyl Alcohol	20.0
Cyclomethicone	15.0
Chromicolor AQ Ink	5.0

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The foregoing description and Examples illustrate selected embodiments of the present invention. In the light thereof variations and modifications will be suggested to one skilled in the art, all of which are within the spirit and  
5 purview of this invention.

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**CLAIMS:**

1. A cosmetic composition comprising:
  - 5 (i) an agent which is capable of interacting with water to a change in the temperature of the cosmetic composition;
  - (ii) a thermochromic substance which changes colour in response to the change of temperature; and
  - 10 (iii) a pharmaceutically acceptable vehicle for delivering the agent and the thermochromic substance to a user's skin.
- 15 2. A composition according to claim 1, wherein the thermochromic substance is a combination of an acid-responsive chromogenic material and an acidic material.
- 20 3. A composition according to claim 1 or claim 2, wherein the thermochromic substance is present at a level of 0.00001 to 10% by weight of the composition.
- 25 4. A composition according to any of the preceding claims, wherein the thermochromic material comprises an acid responsive chromogenic material and an acid material, optionally combined with a solvent.
- 30 5. A composition according to claim 4, wherein the acid-responsive chromogenic material in the thermochromic substance comprises triphenylmethanephthalide compounds, phthalide compounds, phthalan compounds, acyl-leucomethylene blue compounds, fluoran compounds, triphenylmethane

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compounds, diphenylmethane compounds and spiropyran compounds, and mixtures thereof.

6. A composition according to any of the preceding claims,  
5 wherein the acid-responsive chromogenic material is present at a level of 0.1 to 50% by weight of the composition.

7. A composition according to any of the preceding claims,  
wherein the acid material is present at a level of 0.1 to  
10 50% by weight of the composition.

8. A composition according to any of the preceding claims,  
wherein the thermochromic material is microencapsulated.

15 9. A composition according to any of the preceding claims, wherein the agent which is capable of interacting with water is selected from alumina, aluminosilicates, silica and combinations thereof.

20 10. A composition according to claim 9, wherein the exothermic reaction inducing agent is present at a level of 1 to 70% by weight of the composition.



# INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 00/07564

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 A61K7/48

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 97 32567 A (KAO CORPORATION JP.) 12 September 1997 (1997-09-12) Whole document, in particular see on page 19, line 3-11	1-10
Y	WO 93 08793 A (BOOTS CO PLC) 13 May 1993 (1993-05-13) page 2, line 20 - line 28	1-10
Y	DATABASE WPI Section Ch, Week 199902 Derwent Publications Ltd., London, GB; Class A82, AN 1999-012584 XP002155133 & JP 10 265772 A (NICHIBAN KK), 6 October 1998 (1998-10-06) abstract	1-10
	--- -/-	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents:

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Date of the actual completion of the international search

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	FR 2 205 303 A (PIERRET COLETTE) 31 May 1974 (1974-05-31) page 3, line 17 - line 22 claims ----	1
Y	DATABASE WPI Section Ch, Week 198217 Derwent Publications Ltd., London, GB; Class A96, AN 1982-34269E XP002155134 & JP 57 048905 A (KANEBO LTD), 20 March 1982 (1982-03-20) abstract ----	1
A	PATENT ABSTRACTS OF JAPAN vol. 1999, no. 05, 31 May 1999 (1999-05-31) & JP 11 029434 A (KAO CORP), 2 February 1999 (1999-02-02) abstract -----	1

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 00/07564

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9732567 A	12-09-1997	JP 2935343 B JP 11012127 A AU 702300 B AU 2231297 A BR 9707907 A CA 2248326 A CN 1216917 A EP 0904049 A US 6042844 A	16-08-1999 19-01-1999 18-02-1999 22-09-1997 27-07-1999 12-09-1997 19-05-1999 31-03-1999 28-03-2000
WO 9308793 A	13-05-1993	AU 2888292 A	07-06-1993
JP 10265772 A	06-10-1998	NONE	
FR 2205303 A	31-05-1974	BE 806938 A CA 974884 A CH 572743 A DE 2355074 A	01-03-1974 23-09-1975 27-02-1976 06-06-1974
JP 57048905 A	20-03-1982	NONE	
JP 11029434 A	02-02-1999	NONE	